Prepared in cooperation with Rio Blanco County, Colorado

Comparison of Atmospheric Deposition among Three Sites In and Near the Flat Tops Wilderness Area, Colorado, 2003–2005

Scientific Investigations Report 2008–5229

U.S. Department of the Interior
U.S. Geological Survey

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Contents

Figures

Tables

Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square centimeter (cm^2)	0.001076	square foot (ft^2)
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Concentrations of chemical constituents in water are given in microequivalents per liter (µeq/L).

Water year (WY) is defined in this report as the 12-month period October 1 through September 30, designated by the calendar year in which it ends.

Comparison of Atmospheric Deposition among Three Sites In and Near the Flat Tops Wilderness Area, Colorado, 2003–2005

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Abstract

Atmospheric deposition was monitored for ammonium, nitrate, and sulfate concentrations and precipitation amounts in the Flat Tops Wilderness Area of northwestern Colorado at Ned Wilson Lake beginning in 1984 to detect changes that might result from future emissions associated with development of oil-shale resources in northwestern Colorado. Renewed monitoring, by the U.S. Geological Survey, in cooperation with Rio Blanco County, to determine the current status of atmospheric deposition has been ongoing since 2003 at Ned Wilson Lake. Two new monitoring sites were located near Ripple Creek Pass near the Flat Tops Wilderness area and about 12 kilometers north of Ned Wilson Lake because access to the area near Ripple Creek Pass is less difficult and less expensive, particularly in winter and spring. The intent of this study was to establish whether the new deposition data being collected near Ripple Creek Pass, near the northern boundary of the Flat Tops Wilderness Area, would be representative of deposition at sensitive sites within the wilderness such as Ned Wilson Lake and to compare more current (2003 through 2005) deposition data with earlier data (1984 through 1991).

At Ned Wilson Lake, bulk ammonium and nitrate concentrations collected from 1984 through 1991 were similar to those from 2003 through 2005. However, in the same comparison significant differences in sulfate concentrations were observed, indicating a decrease consistent with other regional findings for similar periods. Comparison of concentrations of constituents at two bulk-deposition sites located at Ned Wilson Lake (NWLB) and near Ripple Creek Pass (RCPB) showed only one significant difference ($p = 0.05$) with the winter bulk nitrate concentrations for NWLB significantly lower than winter concentrations from RCPB. Another comparison of concentrations of constituents between the bulk deposition site RCPB and a wet deposition site 100 meters away (RCPW) showed no significant differences for concentrations of ammonium, nitrate, and sulfate for both the winter and summer comparisons. While results indicate many similarities in concentrations of constituents and in seasonal variability in those concentrations, they are based on a short period of study. Precipitation amounts from RCPB were less than the amounts collected at NWLB, and precipitation amounts from RCPW were less than the amounts collected at RCPB. Although RCPB may not be a perfect replacement site for NWLB, it may be similar enough to represent atmospheric deposition in areas of the Flat Tops Wilderness of northwestern Colorado.

Introduction

Energy development and the growth of urban areas in the Rocky Mountain region have increased concern about the environmental effects of atmospheric deposition on high-elevation lakes and streams, particularly in protected areas such as national parks and wilderness areas. Atmospheric deposition monitoring began in the Flat Tops Wilderness Area of northwestern Colorado at Ned Wilson Lake in 1984 (Campbell and others, 1991). Baseline chemistry of atmospheric deposition (including precipitation and dry deposition) and water quality was established to detect changes that might result from future emissions of nitrogen, sulfur, and acidity associated with development of oil-shale resources in northwestern Colorado. Monitoring of atmospheric deposition decreased in the 1990s due to different priorities. During the past two decades, atmospheric emissions and resulting deposition have changed both at regional and at national scales (Fenn and others, 2003a; Lehmann and others, 2005). Currently (2008), there is renewed interest in oil-shale development in northwestern Colorado, and natural gas and oil extraction is increasing in the area. Thus, there is a need for renewed monitoring to determine the current status of atmospheric deposition in the Flat Tops Wilderness Area. Such information is critical to enable resource managers to balance the protection of sensitive resources and economic development.

Currently, nearly all sulfur dioxide (SO_2) emissions and more than 70 percent of nitrogen oxide (NO_x) emissions in the Rocky Mountain region are produced by fossil-fuel combustion in urban areas and by electric utilities (U.S. Environmental Protection Agency, 2006a). SO_2 is of environmental concern because it can be oxidized in the atmosphere to sulfate, which causes visibility impairment and is a major component of acidic deposition (U.S. Environmental

Protection Agency, 2006b). NO_x also is a precursor of pollutants that cause acidic deposition and visibility impairment and produces ozone. Acidic deposition poses a threat to many high-elevation ecosystems in the Rocky Mountains because they are characterized by bedrock and soil types that have little capacity to buffer acidic inputs (Turk and Adams, 1983). Elevated nitrogen deposition to these sensitive ecosystems may provide an additional stress that can lead to changes in soil fertility, shifts in vegetation type, and eutrophication of surface waters (Baron and others, 2000).

Sulfur dioxide emissions have declined in the United States during the 1980s and 1990s, although most strikingly in the East, due to installation of pollution controls at coal-fired generating plants, reductions in emissions from smelters, and reductions in the sulfur content of fuels (U.S. Environmental Protection Agency, 1998). This decline is reflected in decreases in sulfate concentrations in precipitation across the United States for the period 1980 through 1992, including several sites in the Rocky Mountain region (Lynch and others, 1995). Although NO_x emissions also have declined in the Eastern United States, they have increased slightly in the Rocky Mountain region from 1985 through 2002 (Lehmann and others, 2005). In addition, there is increasing concern about emissions of ammonia from agricultural and urban sources adjacent to pristine mountainous areas (Baron and others, 2000). As a result of increasing nitrogen emissions in the Western United States, the relative importance of nitrogen species to precipitation acidity is considerable, and ecological effects of increased deposition of nitrogen may be undesirable (Burns, 2002; Fenn and others, 2003b).

As concerns about potential changes in local and regional atmospheric deposition grow, year-round wet-fall monitoring is no longer possible at sites within the Flat Tops Wilderness Area because of legal and logistical restrictions. Therefore, it is important to establish whether the new deposition data being collected near Ripple Creek Pass, near the northern boundary of the Flat Tops Wilderness Area, are a representative substitute of deposition at sensitive sites within the wilderness such as Ned Wilson Lake. Snowpack and bulk deposition monitoring was restarted at Ned Wilson Lake and near Ripple Creek Pass in water year 2003.

To address this monitoring need, the U.S. Geological Survey (USGS), in cooperation with Rio Blanco County, Colorado, established a program to collect additional deposition samples from annual snowpacks and from bulk and wet-fall collectors at three sites in or near the Flat Tops Wilderness Area. The primary objectives of this program were the following:

1. Determine whether precipitation chemistry data from 2003 through 2005 for Ned Wilson Lake compares to historical data collected during 1984 through 1991 and provide baseline data needed to determine future changes in atmospheric deposition.
2. Compare results of snowpack and bulk precipitation sampling at Ned Wilson Lake to results near Ripple Creek Pass from 2003 through 2005 to evaluate whether the two sites receive comparable atmospheric deposition.
3. Compare results of sampling from 2003 through 2005 snowpack and bulk precipitation for the site near the Ripple Creek Pass National Atmospheric Deposition Program (NADP) site to wet-fall results to determine transferability of the different methods of collecting atmospheric deposition data.

Purpose and Scope

The purpose of this report is to present the statistical comparison of atmospheric deposition among three sites in and near the Flat Tops Wilderness Area, specifically of bulk-deposition and wet-fall chemistry during water years 2003 through 2005, and to present a comparison of results for historical data from 1984 through 1991. This report contains a brief description of sample-collection, analysis, and quality-control methods; volume-weighted mean concentrations of ammonium, nitrate, and sulfate; precipitation amounts; and suggestions for monitoring at three sites in and near the Flat Tops Wilderness Area of Colorado.

Study Area

The three sites compared in this study were located in similar mountainous terrain in alpine and subalpine areas of the White River National Forest in Rio Blanco County in northwestern Colorado (fig. 1). The bulk-deposition monitoring site at Ned Wilson Lake (NWLB) is in a high alpine setting near tree line at about 3,393-m elevation within the Flat Tops Wilderness Area. The bulk-deposition monitoring site located near Ripple Creek Pass (RCPB) is about 12 km north of NWLB and outside the Wilderness Area. The NADP wet-fall site near Ripple Creek Pass (RCPW) is located below tree line in an open meadow adjacent to subalpine forest at about 2,929-m elevation. The nearby bulk-deposition collection site, RCPB, is about 100 m north of RCPW in a similar setting at about 2,938-m elevation. Annual precipitation occurs mostly as snowfall at the three sites, and seasonal snowpacks generally persist from October through April (and as late as July at higher elevations) (Western Regional Climate Center, 2006). The sites generally are upwind from several large powerplants and numerous small emissions sources in the more densely populated areas of eastern Colorado (U.S. Environmental Protection Agency, 2006a).

Data Collection and Analysis

Two periods of data collection are discussed in this report. First, depositional data were collected from 1984 through 1991 at Ned Wilson Lake (Ranalli and others, 1997). Second, depositional data from 2003 through 2005 were collected at the three sites (NWLB, RCPB, and RCPW) using different methods to represent most annual precipitation. Chemical analyses were done to determine concentrations of

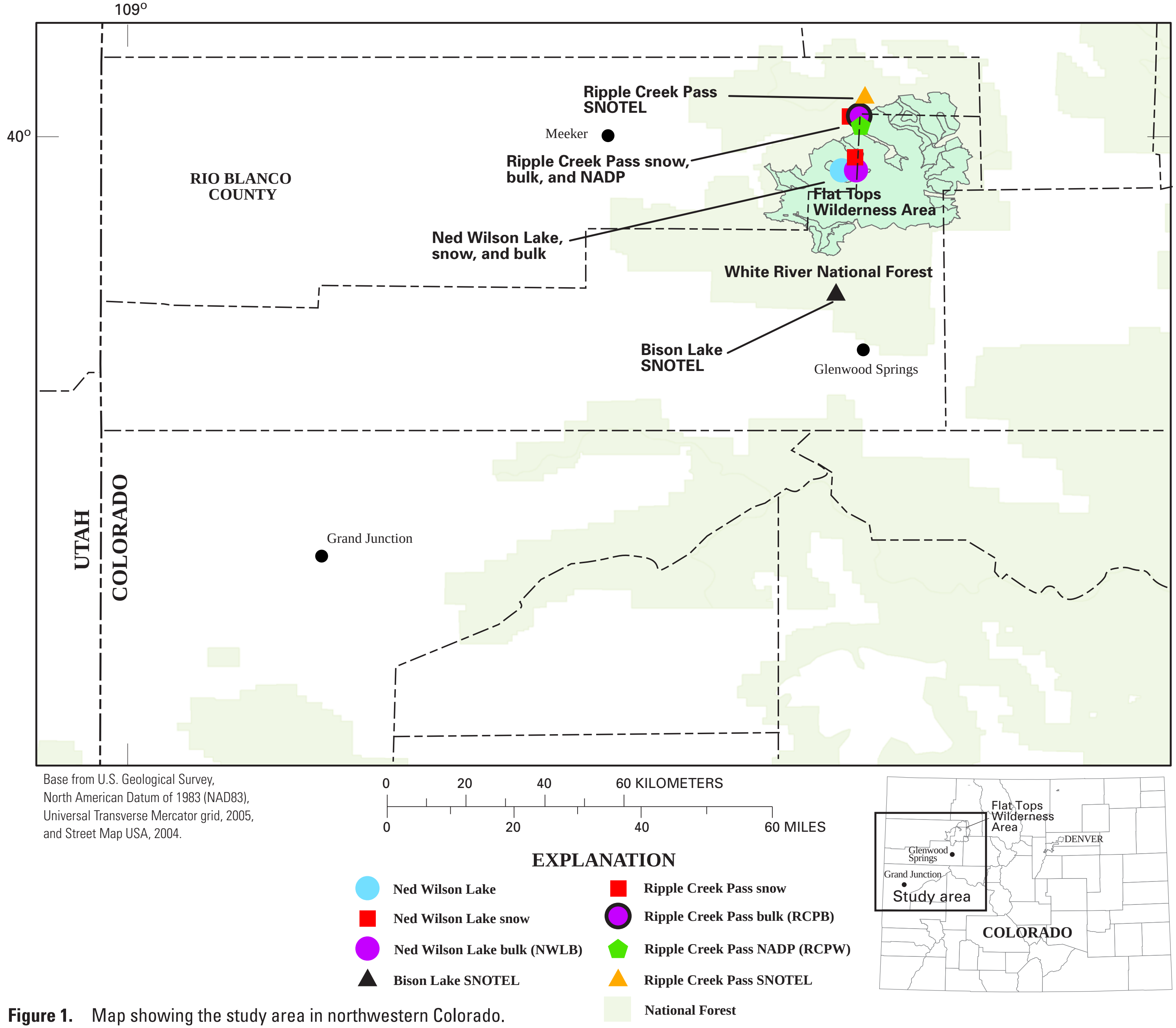

Figure 1. Map showing the study area in northwestern Colorado.

dissolved ammonium, nitrate, and sulfate, and precipitation was measured at each site. Concentrations were statistically compared among the three atmospheric-deposition sites to determine if deposition chemistry at two sites near Ripple Creek Pass (RCPB and RCPW) was representative of deposition chemistry at the Ned Wilson Lake site (NWLB) inside the Flat Tops Wilderness Area. Further comparisons were made of the chemistry of wet-fall samples to either bulk samples or snowpack samples collected near Ripple Creek Pass. Snowpack samples were collected instead of bulk samples during winter when bulk collection was less feasible.

Data Collection

For the data collected during 2003 through 2005, two different methods of sample collection were used to estimate annual atmospheric deposition: (1) seasonal snowpack plus spring and summer bulk precipitation, and (2) wet-fall precipitation. In this report, bulk atmospheric deposition refers to precipitation as snow or rain, and dry deposition (which is occurring constantly). Snowpack is a form of bulk deposition containing both wet and dry deposition from the snow-accumulation period. Wet-fall refers only to water containing dissolved and particulate materials captured during precipitation and does not include dry deposition. Dry deposition is an accumulation of materials deposited from the atmosphere in the absence of precipitation. NADP wet-fall samples include particulate matter deposited exclusively during precipitation events and at no other times. The period of comparison for the study began when the NADP site near Ripple Creek Pass began operation in May 2003 (although snowpack chemical data are included for the previous winter) and continued through October 2005. Volume-weighted-mean (VWM) concentrations were calculated separately as summertime and wintertime periods for the years 2003–2005. The VWM concentration is the product of the precipitation-volume-weighting factor (the sample precipitation volume divided by the sum of all sample precipitation volumes for the period) and the sample concentration.

Seasonal Snowpack

Seasonal snowpack samples were collected to represent precipitation and total (wet and dry, or bulk) deposition that fell from October through April or May (fig. 2). As snowpacks accumulate during the winter and spring, atmospheric deposition occurs during dry periods as well as during periods of precipitation (wet-fall) providing a measurement of total deposition. Because the high-elevation snowpacks in the study area persisted through winter and spring with negligible melt, seasonal snowpack samples offered an efficient medium for collecting naturally composited atmospheric deposition in single samples. Snowpits were prepared and sampled according to USGS protocols before snowmelt began at Ripple Creek Pass (during March or April) and at Ned Wilson Lake (during April or May). Snowpack samples were collected in triplicate during 2005 as a test for precision and small-scale variability (see Appendix). Snowpack-sample collection was done earlier at the RCPB site because snowmelt begins earlier there than at the higher NWLB site. Detailed methods for seasonal snowpack sampling can be found in Ingersoll and others (2002).

Bulk Deposition

To continue collecting year-round wet and dry deposition after the seasonal snowpack began to melt, bulk collectors were deployed at the NWLB and RCPB sites during spring each year. Bulk collectors were installed the same day snowpack samples were collected and were operated until early fall when the next seasonal snowpack began to accumulate, providing a continuous sampling record — all four seasons for each of the 3 years of the study. Bulk collectors were constructed with lightweight materials that could be transported into remote areas efficiently by using skis, snowmobiles, or helicopters. Polyethylene buckets lined with Teflon bags were suspended on steel tripods at heights of 2 to 3 m above the snow or ground surface and were supported with wire-rope guys (fig. 3). Bulk collectors remained open for the duration of the individual sample-collection periods and collected both wet and dry deposition. Individual samples generally were retrieved from the collector at 2- to 3-week intervals, depending upon the amount of precipitation. If inadequate precipitation occurred (less than about 1 L) by the second week, collectors were allowed to remain a third week before samples were retrieved and new Teflon bags installed. During spring, when precipitation could occur as either snowfall or rainfall, 60-L containers were used. Large orifices (1,134 cm^2) and volumes were necessary to capture samples during heavy snowfall common to the area. During summer, when snowfall was less likely, smaller, 20-L buckets with smaller orifices (908 cm^2) replaced the 60-L containers. The 20-L buckets were fitted with funnels to reduce evaporation caused by warmer summertime temperatures. The same collector configuration was used at both the NWLB and RCPB sites. Precipitation collected was calculated as the mass measurement divided by the area of the container orifices.

Wet-Fall Deposition

Wet-fall precipitation data presented in this study were collected by Air Sciences, Incorporated, as part of the National Atmospheric Deposition Program using NADP protocols (National Atmospheric Deposition Program, 2006) at the site near Ripple Creek Pass. Program information and data for the wet-fall site can be found at the NADP Web site at *http://nadp.sws.uiuc.edu/lib* (accessed August 2, 2008). Monthly concentration and precipitation values for the study period were available beginning May 2003 and were exported from the NADP Web site for each month through October 2005. Monthly NADP data were selected for use in this comparison (instead of weekly or seasonal) to more closely resemble the bulk-deposition sampling intervals and to use a similar total

Figure 2. Worker prepares snowpit for full-strata sampling at Ned Wilson Lake in Colorado.

Figure 3. Workers prepare bulk collector near Ripple Creek Pass National Atmospheric Deposition Program site.

number of samples in statistical comparisons to data from the other methods. Monthly NADP data also were used because of the completeness relative to weekly data, which occasionally had missing samples. Monthly values computed by the NADP were thought to be the best available data when weekly data were missing. Although wet-fall- and bulk-sample-collection dates did not exactly coincide, the two sets of sample-collection dates generally matched within 1 to 2 weeks of each other.

A noteworthy distinction about the wet-fall data, when comparing it to bulk-deposition and snowpack data, is that wet-fall data exclude dry deposition, whereas bulk-deposition and snowpack samples contain both wet and dry deposition. The wet-fall collector at RCPW was designed to open the orifice and collect atmospheric deposition only during precipitation events. Once precipitation ceases, the orifice is automatically closed and remains closed until the next precipitation event begins. Thus, wet-fall collection protocol prevents collection of dry atmospheric deposition.

Analytical Methods and Quality Assurance

Concentrations of dissolved ammonium, nitrate, and sulfate in seasonal snowpack and bulk-deposition samples were determined in USGS laboratories in Lakewood, Colorado. Dissolved constituents are defined as those that have passed through a 0.45-micrometer membrane filter. Hereinafter, all concentrations of ammonium, nitrate, and sulfate refer to dissolved concentrations. Seasonal snowpack samples were melted in 8-L Teflon bags used for field collection; bulk-deposition samples were melted in 20- or 60-L Teflon bags used in field collection. Method detection limits were 0.5 µeq/L for ammonium, 0.2 µeq/L for nitrate, and 0.3 µeq/L for sulfate. Ten quality-assurance samples were collected from 2003 through 2005 and included laboratory blanks, field blanks, and field replicates (see Appendix). Concentrations of ammonium, nitrate, and sulfate in field- and laboratory blanks were near or below detection limits in most cases. Small concentrations of nitrate (up to 1.5 µeq/L above the detection limit) were reflected in field blanks. Concentrations of nitrate detected in the field blanks were much lower than concentrations in environmental samples and were not believed to have had a discernible effect on the environmental samples. For comparison of concentrations of selected constituents between environmental samples and replicate samples, relative percent differences (RPD) were calculated. The RPD (expressed as a percentage in this report) is the absolute value of the difference of the environmental sample concentration (E) minus the replicate sample concentration (R), divided by the average of the environmental sample and the replicate sample concentrations, and multiplied by 100 ($|E-R|/[(E+R)/2]) \times 100$). Relative percent differences between collected environmental samples and replicate samples ranged from 0.0 percent to 18.2 percent for ammonium, nitrate, and sulfate. Additional analytical laboratory methods and quality-assurance procedures for analyses of major-ion concentrations are described in Turk and others (2001) and Ingersoll and others (2005). USGS laboratories providing analytical results in this report participated with several other laboratories in continuing performance evaluations of analytical results. Further information about the interlaboratory comparison program for USGS can be found at *http://bqs.usgs.gov/srs#contacts* (accessed December 2, 2008).

Concentrations of dissolved ammonium, nitrate, and sulfate in wet-fall samples were determined using NADP protocols in the Central Analytical Laboratory at the Illinois State Water Survey in Champaign, Illinois. Detection limits reported for NADP wet-fall data for the constituents in this study were similar to those reported for snowpack and bulk deposition. For further information about analytical methods and quality assurance, see *http://nadp.sws.uiuc.edu/* (accessed August 2, 2008).

Statistical Methods

For the historical data comparison, data from 1984 through 1991 for NWLB for precipitation, and bulk ammonium, nitrate, and sulfate concentrations were compared to data from 2003 through 2005 for the same site. The Wilcoxon rank-sum test was used to test for differences among the variables (Wilcoxon, 1945; Iman and Conover, 1983).

For the more recent data comparisons, two hypotheses were evaluated at three sites: (1) volume-weighted mean bulk concentrations at NWLB were different from VWM bulk concentrations at RCPB, and (2) VWM bulk concentrations at RCPB were different from NADP VWM wet-fall concentrations at RCPW. Distributions of concentrations mostly were non-normal during the study at the three monitoring sites (NWLB, RCPB and RCPW), so nonparametric statistical tests were used to evaluate differences between concentration data from site to site. The Wilcoxon rank-sum test was performed to compare volume-weighted mean concentrations of ammonium, nitrate, and sulfate among the three sites for the study period. For example, for a given constituent observed, such as ammonium concentrations, all concentrations for NWLB and RCPB first were divided into either the winter or summer group. At RCPB, the winter grouping generally included the period October through May, and the summer grouping generally included the period June through September (or October depending upon the onset of the snowfall season). At the higher elevation NWLB site, winterlike conditions often persist until July. So, the winter grouping there generally included the period October through June, and the summer grouping generally included the period July through September. Using these seasonal groupings, VWM bulk ammonium concentrations for NWLB were tested against VWM bulk ammonium concentrations for RCPB. Next, seasonally selected VWM concentrations for RCPB were tested against seasonal VWM-wetfall-ammonium concentrations for RCPW. One-tailed tests were used to determine if concentration or precipitation were greater or lesser at one of two sites being compared. In this report, p-values of 0.05 indicate a significant difference, p-values of 0.20 indicate weak significant difference, and p-values above 0.20 indicate no significant difference.

Atmospheric Deposition Chemistry

Concentration and precipitation results for the NWLB, RCPB, and RCPW sites are presented in tables 1, 2, and 3, respectively. Concentrations of dissolved ammonium, nitrate, and sulfate and precipitation amounts are shown for each sample collected for the comparison. Seasonal volume-weighted mean concentrations were calculated for two general groups: wintertime and summertime samples (table 4). Precipitation samples including both snowpack and bulk-deposition samples were collected at NWLB and RCPB sites by using the same methods throughout the period May 2003 through October 2005. The two complete water years (WY) of the period (2004 and 2005) were represented by a series of samples starting with seasonal snowpack samples collected in March or April (which had begun to accumulate during the previous fall) and ending with bulk-deposition samples collected through summer and into October. In all, 17 samples were collected at NWLB and 31 samples were collected at RCPB. Wet-fall samples at RCPW were collected differently but represent wet deposition during most of the same time period. Wet-fall collection began during May 2003 and continued through October 2005, for a total of 30 months. It is important to point out that these results are based on a limited sample set, and comparisons would be more robust if more data were available.

Table 1. Dissolved concentrations and volume-weighted-mean concentrations of ammonium, nitrate, and sulfate and precipitation amounts in winter and summer bulk-deposition samples collected at Ned Wilson Lake in Colorado (NWLB) 2003 through 2005.

[μeq/L, microequivalents per liter; VWM, volume-weighted mean; cm, centimeters; na, not applicable]

Sampling period	Collection date	Ammonium as NH_4^+ (μeq/L)	Nitrate as NO_3^- (μeq/L)	Sulfate as SO_4^{2-} (μeq/L)	Precipitation (cm)
Winter[1,2]	5/13/2003	5.4	9.3	6.1	97.7
Winter	6/25/2003	23.7	28.2	28.5	1.6
Seasonal VWM[3]		5.7	9.6	6.5	na
Winter	4/13/2004	3.7	7.2	3.7	75.6
Winter	7/11/2004	10.1	44.6	34.2	5.9
Seasonal VWM		4.2	9.9	5.9	na
Winter	4/22/2005	3.7	7.0	4.5	98.3
Winter	7/13/2005	18.8	24.6	24.4	12.3
Seasonal VWM		5.4	9.0	6.7	na
Summer[4]	8/27/2003	16.5	31.5	17.9	5.8
Summer	9/17/2003	8.2	15.0	8.7	2.9
Seasonal VWM		13.8	26.0	14.8	na
Summer	7/26/2004	7.5	17.6	8.4	4.2
Summer	8/9/2004	26.9	40.1	25.8	1.4
Summer	8/21/2004	14.0	21.1	14.9	1.9
Summer	9/29/2004	10.6	16.4	12.9	9.6
Seasonal VWM		11.6	19.2	13.1	na
Summer	8/13/2005	13.7	14.7	9.4	9.5
Summer	8/24/2005	17.6	19.7	16.1	3.5
Summer	9/9/2005	12.8	19.9	17.9	3.5
Summer	9/25/2005	4.4	12.6	11.0	1.1
Summer	10/12/2005	6.2	7.1	9.3	5.2
Seasonal VWM		12.0	14.4	11.8	na

[1]Sample concentrations (ammonium, nitrate, and sulfate) and precipitation amounts collected by sample.

[2]Winter season generally was grouped as October through June.

[3]Seasonal VWM shown for ammonium, nitrate, and sulfate.

[4]Summer season generally was grouped as July through September.

Table 2. Dissolved concentrations and volume-weighted-mean concentrations of ammonium, nitrate, and sulfate, and precipitation amounts in winter and summer bulk-deposition samples collected near Ripple Creek Pass in Colorado (RCPB) 2003 through 2005.

[µeq/L, microequivalents per liter; VWM, volume-weighted mean; cm, centimeters; na, not applicable]

Sampling period	Collection date	Ammonium as NH_4^+ (µeq/L)	Nitrate as NO_3^- (µeq/L)	Sulfate as SO_4^{2-} (µeq/L)	Precipitation (cm)
Winter[1,2]	04/04/2003	4.6	11.0	5.7	66.1
Winter	05/14/2003	9.1	13.5	11.9	23.1
Winter	06/03/2003	25.9	28.5	21.1	1.5
Seasonal VWM[3]		6.1	12.0	7.5	na
Winter	04/01/2004	4.3	10.9	4.7	82.9
Winter	05/25/2004	0.0	28.0	24.5	4.4
Seasonal VWM		4.1	11.8	5.7	na
Winter	03/28/2005	4.5	9.4	6.3	48.2
Winter	05/09/2005	11.2	14.2	13.5	6.9
Winter	06/07/2005	11.5	15.8	15.2	9.7
Seasonal VWM		6.2	10.9	8.4	na
Summer[4]	06/23/2003	72.6	26.2	32.2	1.8
Summer	07/29/2003	42.9	52.2	44.2	0.9
Summer	08/26/2003	13.9	15.6	7.7	3.1
Summer	09/02/2003	19.3	27.8	15.2	1.4
Summer	09/22/2003	5.9	16.4	15.8	5.6
Seasonal VWM		21.1	21.3	18.0	na
Summer	06/26/2004	5.3	13.2	25.5	3.3
Summer	07/07/2004	39.9	16.1	15.1	2.8
Summer	07/17/2004	7.4	30.8	13.7	1.2
Summer	07/27/2004	13.9	25.9	11.7	1.1
Summer	08/10/2004	33.5	45.4	28.2	1.1
Summer	08/31/2004	13.1	18.7	15.0	6.8
Summer	09/13/2004	32.4	52.1	27.9	0.5
Summer	09/28/2004	8.3	10.7	8.5	6.3
Summer	09/28/2004	8.3	10.6	8.3	6.3
Summer	10/19/2004	8.2	15.8	11.7	4.3
Seasonal VWM		12.9	16.6	13.6	na
Summer	06/21/2005	3.8	12.1	7.2	2.6
Summer	07/12/2005	16.4	31.0	34.6	2.1
Summer	07/26/2005	8.6	16.3	11.5	2.5
Summer	08/02/2005	36.5	32.8	23.3	0.5
Summer	09/06/2005	4.3	21.5	15.9	3.9
Summer	09/27/2005	0.9	14.3	12.6	3.1
Summer	10/18/2005	0.1	0.0	8.8	6.1
Summer	11/08/2005	2.1	12.9	10.5	3.2
Seasonal VWM		4.7	13.5	13.3	na

[1]Sample concentrations (ammonium, nitrate, and sulfate) and precipitation amounts collected by sample.

[2]Winter season generally was grouped as October through May.

[3]Seasonal VWM shown for ammonium, nitrate, and sulfate.

[4]Summer season generally was grouped as June through October.

Table 3. Dissolved concentrations and volume-weighted-mean concentrations of ammonium, nitrate, and sulfate and precipitation amounts at NADP wet-fall site near Ripple Creek Pass in Colorado (RCPW), 2003 through 2005.

[µeq/L, microequivalents per liter; VWM, volume-weighted mean; cm, centimeters; na, not applicable]

Sampling period	Month	Year	Ammonium as NH_4^+ (µeq/L)	Nitrate as NO_3^- (µeq/L)	Sulfate as SO_4^{2-} (µeq/L)	Precipitation (cm)
Winter[1,2]	May	2003	18.9	16.3	16.0	3.0
Seasonal VWM[3]			18.9	16.3	16.0	na
Winter	Oct[4]	2003	15.0	23.4	16.3	0.4
Winter	Nov	2003	12.4	12.4	9.7	11.8
Winter	Dec	2003	2.7	7.9	4.5	5.0
Winter	Jan	2004	2.2	7.5	2.0	5.2
Winter	Feb	2004	2.1	8.7	4.7	5.1
Winter	Mar	2004	13.0	22.4	16.2	3.9
Winter	Apr	2004	8.9	8.9	7.0	7.6
Winter	May	2004	8.5	14.9	11.7	3.9
Seasonal VWM			7.9	11.5	7.9	na
Winter	Nov	2004	2.0	6.1	4.2	5.2
Winter	Dec	2004	8.8	10.5	3.4	2.0
Winter	Jan	2005	0.9	6.9	2.3	6.4
Winter	Feb	2005	4.1	8.6	5.3	4.1
Winter	Mar	2005	5.7	7.1	6.8	4.5
Winter	Apr	2005	4.6	6.7	5.8	7.9
Winter	May	2005	7.3	10.7	11.4	5.2
Seasonal VWM			4.3	7.7	5.7	na
Summer[5]	June	2003	29.9	26.5	27.3	3.3
Summer	July	2003	48.1	34.3	25.0	1.0
Summer	Aug	2003	18.0	18.2	10.5	9.0
Summer	Sept	2003	7.8	9.5	6.3	1.9
Seasonal VWM			21.3	20.0	14.6	na
Summer	June	2004	21.7	27.6	21.3	2.7
Summer	July	2004	9.9	12.7	8.3	5.1
Summer	Aug	2004	10.7	16.8	13.2	4.4
Summer	Sept	2004	6.2	8.5	8.1	8.8
Summer	Oct	2004	3.3	8.2	6.2	8.6
Seasonal VWM			8.1	12.1	9.5	na
Summer	June	2005	10.6	12.6	12.4	11.6
Summer	July	2005	15.7	17.3	13.7	4.2
Summer	Aug	2005	9.7	14.9	10.9	5.6
Summer	Sept	2005	7.0	10.1	9.6	3.7
Summer	Oct	2005	5.4	6.4	8.0	9.2
Seasonal VWM			9.3	11.6	10.8	na

[1]Sample concentrations (ammonium, nitrate, and sulfate) and precipitation amounts collected by sample.

[2]Winter season generally was grouped as October through May.

[3]Seasonal VWM shown for ammonium, nitrate, and sulfate.

[4]The October sample in 2003 was included in the winter grouping so that the end of the Summer 2003 sampling period in this table would correspond to the end of the summer sampling period in 2003 at RCPB (09/22/2003, table 2).

[5]Summer season generally was grouped as June through October.

Table 4. Summary of seasonal volume-weighted mean concentrations for dissolved ammonium, nitrate, and sulfate at study sites, 2003 through 2005.

[Units in microequivalents per liter; NWLB, bulk deposition at Ned Wilson Lake in Colorado; RCPB, bulk deposition near Ripple Creek Pass in Colorado; RCPW, wet fall at NADP site near Ripple Creek Pass in Colorado]

Constituent and site	Winter 2003	Winter 2004	Winter 2005	Winter average	Summer 2003	Summer 2004	Summer 2005	Summer average
Ammonium as NH_4^+								
NWLB	5.7	4.2	5.4	5.1	13.8	11.6	12.0	12.5
RCPB	6.1	4.1	6.2	5.5	21.1	12.9	4.7	12.9
RCPW	18.9	7.9	4.3	10.3	21.3	8.1	9.3	12.9
Nitrate as NO_3^-								
NWLB	9.6	9.9	9.0	9.5	26.0	19.2	14.4	19.9
RCPB	12.0	11.8	10.9	11.5	21.3	16.6	13.5	17.1
RCPW	16.3	11.5	7.7	11.8	20.0	12.1	11.6	14.6
Sulfate as SO_4^{2-}								
NWLB	6.5	5.9	6.7	6.4	14.8	13.1	11.8	13.2
RCPB	7.5	5.7	8.4	7.2	18.0	13.6	13.3	15.0
RCPW	16.0	7.9	5.7	9.9	14.6	9.5	10.8	11.7

Chemical Concentrations

Three comparisons of results of atmospheric-deposition monitoring were performed in this study. First, historical data for precipitation and bulk deposition at NWLB were compared to more recent data collected at the same site. Second, comparisons between the two bulk-deposition sites, NWLB and RCPB, were done with data collected during similar time periods. These comparisons were done to evaluate whether bulk-deposition data collected near the more accessible RCPB site were different from bulk-deposition data from the remote site within the Flat Tops Wilderness Area at NWLB. Third, bulk-deposition data from RCPB were compared to wet-fall data at nearby RCPW as a test of comparability of different methods.

Data for precipitation and bulk ammonium, nitrate, and sulfate concentrations for the Ned Wilson site from 2003 through 2005 were compared to data from the same site from 1984 through 1991, which were collected using the same sampling and analytical methods. Nearly all of the samples from the earlier period were collected during the early summer through early fall and did not contain winter samples that could be compared to the winter samples collected during the 2003 through 2005 period. Therefore, the comparison between periods was made only for samples collected during the early summer through early fall timeframe (June through October).

Volume-weighted mean bulk sulfate concentration was the only variable that differed significantly between the two periods. The Wilcoxon rank-sum test (Wilcoxon, 1945; Iman and Conover, 1983), which was used to test for differences, showed the sulfate concentration for the recent period was significantly less than that for the earlier period ($p = 0.02$). The p-value indicates a 2-percent random chance of finding the same difference in concentrations from the same population. The VWM sulfate bulk concentration for the recent period ($n = 3$) was 13.1 μeq/L compared to 16.9 μeq/L ($n = 8$) for the earlier period. This difference is consistent with other regional analyses showing a general decline in atmospheric sulfate deposition resulting from implementation of increasingly more stringent emission standards on coal-fired electric plants (Nilles and Conley, 2001; Lehmann and others, 2005).

The second set of comparisons was made between the two bulk-deposition sites, NWLB and RCPB. Samples were grouped by wintertime or summertime collection, and volume-weighted mean concentrations were calculated for each group (figs. 4 A–C). Results indicated little significant difference in concentrations of ammonium, nitrate, or sulfate (table 5). Wintertime nitrate concentrations at NWLB were significantly lower ($p = 0.05$) than concentrations from RCPB, and summertime sulfate concentrations at NWLB were lower than concentrations at RCPB but were weakly significant ($p = 0.20$). However, seasonal fluctuations resulting in higher concentrations during summer were reflected in seasonal averages for all three constituents for both NWLB and RCPB (table 4). Consistent with the seasonal fluctuations noted, the significantly lower winter nitrate concentration at NWLB matches the pattern of lower wintertime concentration at both sites. Although these results suggest that seasonal concentrations of ammonium, nitrate, and sulfate at NWLB generally were similar to those at RCPB, the small sample size from 3 years of data limits confidence because it is uncertain if these sample values are representative of the larger population.

Table 5. Wilcoxon rank-sum test results shown as p-values for three monitoring sites for seasonal volume-weighted-mean concentrations of ammonium, nitrate, and sulfate in atmospheric deposition samples.

[Values shown in bold are significant at p=0.05 level; p-values shown in italics indicate weak significance (p=0.20); NWLB, bulk deposition at Ned Wilson Lake in Colorado; RCPB, bulk deposition near Ripple Creek Pass in Colorado; RCPW, wet-fall at NADP site near Ripple Creek Pass, Colorado]

H_a: x>y[1]	**NWLB compared to RCPB**		**RCPB compared to RCPW**	
	Winter	Summer	Winter	Summer
Ammonium	0.80	0.65	0.65	0.65
Nitrate	1.00	0.35	0.35	*0.20*
Sulfate	0.80	0.90	0.35	*0.20*
H_a: x<y	**NWLB compared to RCPB**		**RCPB compared to RCPW**	
	Winter	Summer	Winter	Summer
Ammonium	0.35	0.50	0.50	0.50
Nitrate	**0.05**	0.80	0.80	0.90
Sulfate	0.35	*0.20*	0.80	0.90

[1] P-values for alternate hypotheses of NWLB > RCPB or RCPB > RCPW (H_a: x>y), and NWLB < RCPB or RCPB < RCPW (H_a: x<y) are results of 1-tailed Wilcoxon rank-sum tests.

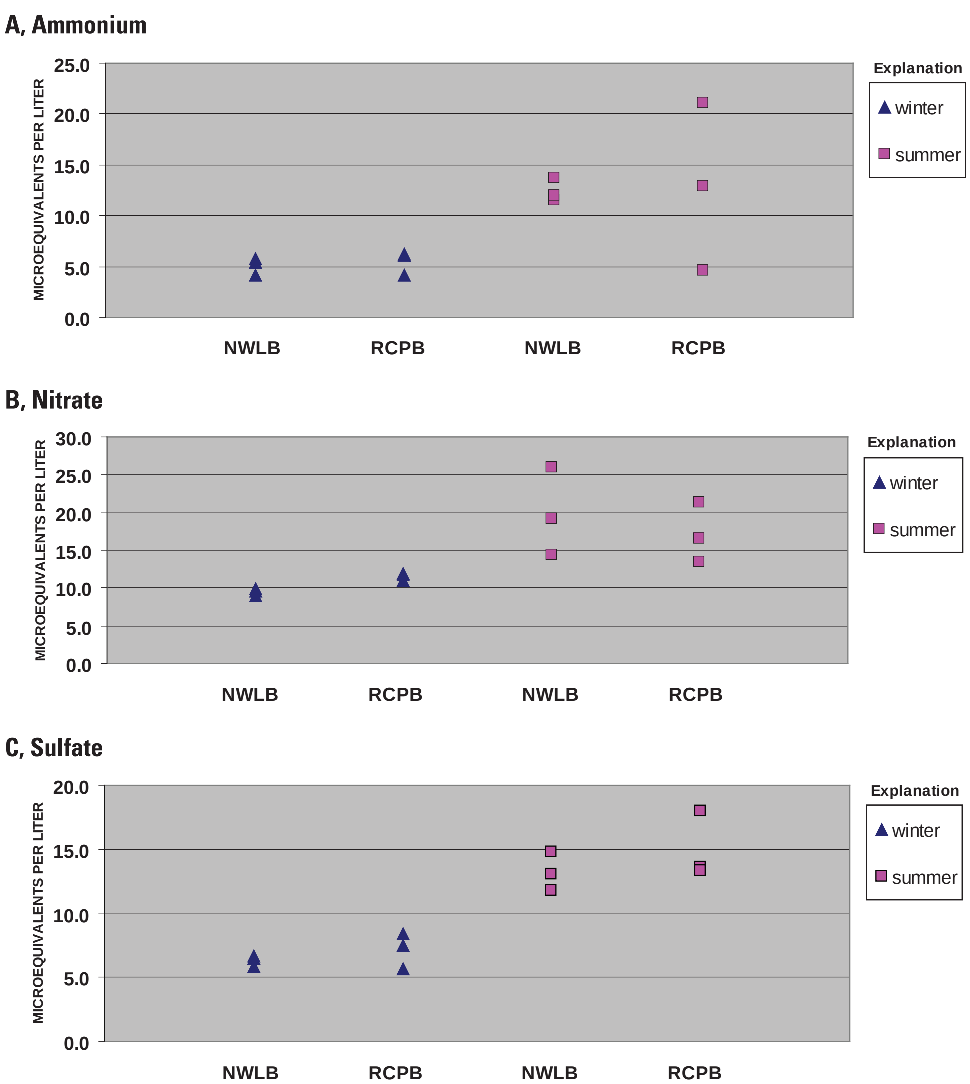

Figure 4. Seasonal volume-weighted-mean concentrations of (A) ammonium, (B) nitrate, and (C) sulfate in bulk deposition at the Ned Wilson Lake site (NWLB) compared to the Ripple Creek Pass site (RCPB). Winter pair is on the left and summer pair is on the right.

The third set of comparisons was made between RCPB and RCPW (figs. 5A–C). Bulk samples at RCPB for the period before the wet-fall collector became operational in mid-May 2003 at RCPW (collection dates of 04/04/03 and 05/14/03 [table 2]) were excluded from figures 5A–C in order to match the initial date of collection at RCPW. Thus, different seasonal, volume-weighted means for RCPB were used in the comparison between RCPB and RCPW (25.9 µeq/L of ammonium, 28.5 µeq/L of nitrate, and 21.1 µeq/L of sulfate) (table 2; figs. 5A–C) than were used for the comparison between NWLB and RCPB (6.1 µeq/L of ammonium, 12.0 µeq/L of nitrate, and 7.5 µeq/L of sulfate) (table 2; figs. 4A–C).

Results for both the winter and summer seasons showed no difference between ammonium concentrations but showed weakly significant differences between nitrate ($p = 0.20$) and sulfate ($p = 0.20$) concentrations during the summer seasons (table 5). Wet-fall collection may have been affected by the exclusion of dry deposition during periods of no precipitation, particularly with nitrate and sulfate. Generally, somewhat higher concentrations of nitrate and sulfate at RCPB compared to RCPW were consistent with the inclusion of dry deposition in bulk samples. Previous work at the NWLB site indicated consistently higher concentrations in bulk compared to wet-fall samples collected side-by-side (Ranalli and others, 1997). Other analysis of total deposition data for ammonium, nitrate, and sulfate also indicated the importance of dry deposition in the region (Clow and others, 2002). Further, dry deposition monitored in the Rocky Mountain region from 2002 to 2004 by the Clean Air Status and Trends Network (CASTNet) program constituted a substantial fraction of total atmospheric deposition in Colorado, particularly during summertime (National Park Service, 2007). However, dry deposition of ammonium at six CASTNet sites in the Rocky Mountain region was small relative to dry deposition of nitrate or sulfate (U.S. Environmental Protection Agency, 2007). This is one explanation why there were generally higher concentrations in bulk samples for nitrate and sulfate but not for ammonium. This comparison suggests that wet-fall deposition chemistry monitored near Ripple Creek Pass may not fully represent total deposition (for nitrate and sulfate, in particular).

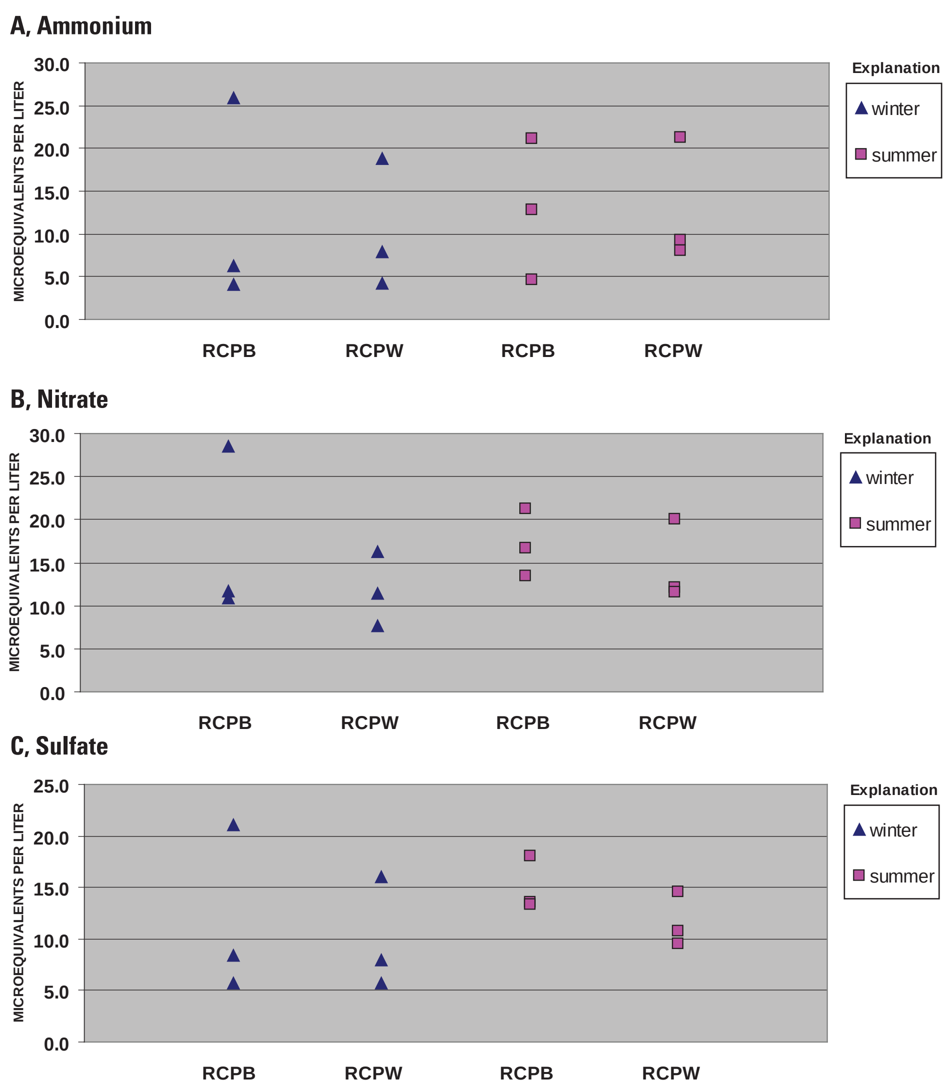

Figure 5. Seasonal volume-weighted-mean concentrations of (A) ammonium, (B) nitrate, and (C) sulfate at the Ripple Creek Pass bulk deposition site (RCPB) compared to Ripple Creek Pass wet deposition site (RCPW). Winter pair is on the left and summer pair is on the right.

Precipitation Amounts

Total annual precipitation amounts at sampling sites and nearby snow telemetry (SNOTEL) sites, operated by the U.S. Department of Agriculture Natural Resources Conservation Service (Western Regional Climate Center, 2006), were measured or modeled during the study for the complete water years 2004 and 2005 (table 6). Two SNOTEL sites in the general area (within 45 km) recorded annual precipitation during the study at comparable elevations in mountainous terrain. SNOTEL sites at Ripple Creek Pass and Bison Lake (fig. 1) reported similar ranges of total annual precipitation as compared to those of NWLB and RCPB. However, considerably less precipitation was recorded for RCPW. In common with the bulk-deposition site at NWLB, the Bison Lake SNOTEL site is at a higher elevation (3,316 m) than the Ripple Creek Pass SNOTEL site (3,151 m). For additional comparison, modeled estimates of annual precipitation for WY 2004 and WY 2005 for NWLB and RCPB are available from the PRISM (Parameter-elevation Regressions on Independent Slopes Model) Group (2007). PRISM estimates also are in the same general range of measured precipitation amounts but were not always in close agreement. In all cases, the 2005 precipitation was greater than the 2004 precipitation except for RCPB. At the Ripple Creek Pass SNOTEL site, total annual precipitation was below the 30-year average of 118 cm in 2004 (94 cm) and in 2005 (98 cm). At the Bison Lake SNOTEL site, total annual precipitation was below the 30-year average of 117 cm in 2004 (106 cm) and above average in 2005 (128 cm). According to 30-year averages for 1971 through 2000 at the SNOTEL sites, the study period was characterized both by wet and by dry periods, but few extreme deviations from average were noted. However, dry periods occurred during summer, especially during 2003, and limited the number of precipitation samples. This explains the relative shortage of bulk-deposition samples both at RCPB and NWLB and also is reflected in reduced precipitation amounts and wet-fall samples that year at RCPW.

For the comparison between NWLB and RCPB, total precipitation for water year 2004 and water year 2005 was 11 percent greater at NWLB (as would be expected of the higher elevation site). However, in the comparison between RCPB and RCPW, total precipitation for the same period was substantially higher (58 percent) at RCPB, particularly in winter. There are three likely explanations for this. First, annual precipitation measured in 2004 at RCPB (120.9 cm) was greater than would be expected because the snowpack water content was much higher at the nearby alternate location chosen. The 2004 snowpack site was relocated about 200 m east of the RCPB site, at a similar elevation, due to early snowmelt at the original site. Relocation of the snowpack-sampling site to a steeper site with less exposure to the sun was necessary to collect the annual snowpack sample intact. A second explanation for this difference likely is the undercatch at the gage at the NADP site, a common problem in precipitation measurement (Goodison and others, 1998; Yang and others, 2000). Last, the larger amount of precipitation also was due to the large fraction of winter precipitation at RCPB that was represented by the annual snowpack and the tendency for undercatch in gages to be highest in winter due to blowing snow. For these reasons, precipitation measurements from SNOTEL sites, or modeled precipitation estimates for the study area, may be more useful for calculation of wet deposition.

NWLB is about 455 m higher in elevation than RCPB, which may account for the larger amounts of precipitation collected at NWLB. Given the general similarities in constituent concentrations, it is reasonable to assume that data collected from the two sites are from similar, but not identical, populations.

Table 6. Location information and measured and modeled annual precipitation amounts at sampling sites and nearby SNOTEL sites.
[Latitude (north) and Longitude (west) in decimal degrees; m, meters; cm, centimeters; NWLB, bulk deposition at Ned Wilson Lake in Colorado; RCPB, bulk deposition near Ripple Creek Pass in Colorado; RCPW, wet fall at NADP site near Ripple Creek Pass in Colorado; SNOTEL, snow-telemetry site]

Site	Latitude	Longitude	Elevation (m)	Annual precipitation (cm)	
				Water year 2004	Water year 2005
NWLB	39.9608	107.3214	3,393	98.6	133.4
NWLB[1]	39.9608	107.3214	3,393	95.7	102.8
RCPB	40.0861	107.3119	2,938	120.9	88.8
RCPB[1]	40.0861	107.3119	2,938	93.8	96.1
RCPW	40.0851	107.3118	2,929	63.9	69.0
Bison Lake SNOTEL	39.7600	107.3600	3,316	106.4	127.5
Ripple Creek Pass SNOTEL	40.1100	107.2900	3,151	94.5	98.0

[1]Estimated from modeled information (PRISM Group, 2007).

Summary and Conclusions

The U.S. Geological Survey has been monitoring bulk atmospheric deposition of ammonium, nitrate, and sulfate intermittently at a site at Ned Wilson Lake (NWLB) in the Flat Tops Wilderness Area since 1984. This site is key to monitoring the impacts of oil-shale development and the continuing expansion of gas and oil development on atmospheric deposition in northwestern Colorado. For many reasons, it is no longer feasible to continue operating the Ned Wilson Lake site. In 2003 a potential substitute bulk atmospheric deposition monitoring site (RCPB) and a wet-deposition monitoring site (RCPW) were established near Ripple Creek Pass just outside of the Flat Tops Wilderness Area. The U.S. Geological Survey, in cooperation with Rio Blanco County, Colorado, established a program to determine if atmospheric deposition of ammonium, nitrate, and sulfate from 2003 through 2005 at NWLB compares to historical data collected during 1984 through 1991; to determine if bulk atmospheric deposition data at the NWLB site are similar to that collected at the RCPB site; and to compare bulk atmospheric deposition chemistry and wet-deposition chemistry collected at the RCPB and RCPW, respectively.

For the comparison of VWM bulk ammonium, nitrate, and sulfate concentrations collected from 1984 through 1991 to those from 2003 through 2005, the Wilcoxon rank-sum test showed only a significant difference in sulfate concentrations. The sulfate concentration for the 2003 through 2005 period was significantly lower than that for the 1984 through 1991 period, which is consistent with other regional findings for similar periods.

For comparison of the VWM concentrations of constituents at the bulk sites, NWLB and RCPB, seasonal variations in VWM concentrations of ammonium and sulfate were similar for the two sites. The Wilcoxon rank-sum test showed only one significant difference ($p = 0.05$): the winter bulk nitrate concentrations for NWLB were significantly lower than winter concentrations from RCPB. Summer bulk VWM concentrations of sulfate also tended to be lower at NWLB, but at a weak level of significance ($p = 0.20$). Because only three VWM concentrations were used for each of the winter and for each of the summer statistical comparisons of bulk concentrations, these results may not be representative of the larger, unsampled population of concentrations.

The statistical comparison of VWM concentrations of constituents between the bulk deposition site (RCPB) and the wet deposition site (RCPW), showed no significant differences for concentrations of ammonium, nitrate, and sulfate for both the winter and summer comparisons. Summer VWM concentrations of nitrate and sulfate from RCPB tended to be higher than concentrations from RCPW but at a weak level of significance ($p = 0.20$). Further, the bulk VWM concentrations for nitrate and sulfate showed generally higher ranges of concentrations than those associated with the wet deposition, which indicates that the RCPW does not represent the full spectrum of atmospheric deposition. Note that slightly different VWM concentrations were used for these comparisons for 2003 because the RCPW site did not begin collecting data until mid-May of that year, and the bulk samples collected in April and early May 2003 were not used in the comparison.

Precipitation amounts from NWLB were greater than the amounts collected at RCPB, probably because of the difference in elevations. Precipitation amounts from RCPB were greater than the amounts collected at RCPW. The comparison of RCPB and RCPW precipitation amounts was confounded by the need to temporarily relocate the snowpack site in 2004. Also, wet-fall collectors tend to undercollect precipitation. For these reasons, precipitation measurements from SNOTEL sites, or modeled precipitation estimates for the study area, may be more useful for calculation of wet deposition.

Although data were not available to generate truly rigorous statistical comparisons of the NWLB and RCPB data, the statistical results indicate many similarities in VWM concentrations of constituents and in seasonal variability in those concentrations. Also, NWLB is about 455 m higher in elevation than RCPB, which may account for some of the larger amounts of precipitation collected at NWLB relative to RCPB. Given the general similarities, it is reasonable to assume that data collected from the two sites are from similar, but not identical, populations. Further, although RCPB is not a perfect replacement site for NWLB, it may be similar enough to represent atmospheric deposition in northwestern Colorado.

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Appendix

Quality-assurance data for laboratory blanks, field blanks, and field replicates.

[μeq/L, microequivalents per liter; RPD, relative percent difference; DFC, Denver Federal Center, Lakewood, Colo.; NWLB, bulk-deposition at Ned Wilson Lake in Colorado; RCPB, bulk-deposition near Ripple Creek Pass in Colorado; bulk, summertime bulk collector; snow, wintertime snowpack; <, less than; na, not applicable]

			Ammonium, dissolved, as NH_4^+		Nitrate, dissolved, as NO_3^-		Sulfate, dissolved, as SO_4^{2-}	
Sample type	Site name	Collect date	(μeq/L)	RPD	(μeq/L)	RPD	(μeq/L)	RPD
Laboratory blank	DFC	09/18/2003	<0.5	na	<0.2	na	<0.3	na
Laboratory blank	DFC	06/04/2004	<0.5	na	<0.2	na	<0.3	na
Field blank	NWLB (bulk)	08/21/2004	<0.5	na	1.6	na	<0.3	na
Field blank	NWLB (bulk)	07/23/2005	<0.5	na	1.7	na	<0.3	na
Environmental	NWLB (snow)	04/22/2005	3.7	na	7.0	na	4.5	na
Field replicate	NWLB (snow)	04/22/2005	3.3	11.3	7.8	11.0	4.9	7.6
Field replicate	NWLB (snow)	04/22/2005	3.1	17.2	6.3	10.1	4.6	1.1
Field blank	RCPB (bulk)	09/22/2003	<0.5	na	0.3	na	<0.3	na
Environmental	RCPB (bulk)	09/28/2004	8.3	na	10.7	na	8.5	na
Field replicate	RCPB (bulk)	09/28/2004	8.3	0.0	10.6	0.9	8.3	2.4
Environmental	RCPB (snow)	03/28/2005	4.5	na	9.4	na	6.3	na
Field replicate	RCPB (snow)	03/28/2005	4.9	9.0	9.2	3.1	6.5	2.5
Field replicate	RCPB (snow)	03/28/2005	4.0	10.6	8.2	13.9	5.2	18.2

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